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# The Global Atmosphere Watch reactive gases measurement network

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## Abstract

Long-term observations of reactive gases in the troposphere are important for understanding trace gas cycles and the oxidation capacity of the atmosphere, assessing impacts of emission changes, verifying numerical model simulations, and quantifying the interactions between short-lived compounds and climate change. The World Meteorological Organization's (WMO) Global Atmosphere Watch (GAW) program coordinates a global network of surface stations some of which have measured reactive gases for more than 40 years. Gas species included under this umbrella are ozone, carbon monoxide, nitrogen oxides, and volatile organic compounds (VOCs). There are many challenges involved in setting-up and maintaining such a network over many decades and to ensure that data are of high quality, regularly updated and made easily accessible to users. This overview describes the GAW surface station network of reactive gases, its unique quality management framework, and discusses the data that are available from the central archive. Highlights of data use from the published literature are reviewed, and a brief outlook into the future of GAW is given. This manuscript constitutes the overview of a special feature on GAW reactive gases observations with individual papers reporting on research and data analysis of particular substances being covered by the program.

## 1. Introduction

Reactive gas species in the Earth's lower atmosphere are a large group of substances with lifetimes between hours and a few months. They are the primary source of the highly reactive atomic and free radical species that drive the gas phase chemistry of the atmosphere. This radical chemistry is essential for cleansing the atmosphere of a range of pollutants and greenhouse gases by initiating the oxidation of reduced compounds. Key reactive gases, which are also readily measurable, are tropospheric ozone, carbon monoxide, volatile organic compounds, reactive nitrogen gases, and reactive sulfur gases. Reactive gases play a dual role in the

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Earth's atmosphere. Firstly, they impact the climate system. Some species are direct greenhouse gases, while others have a strong effect on the oxidation processes which control the chemical lifetime of other greenhouse gases including methane. Indirect climate impacts are also exerted through reactive hydrocarbons emitted by vegetation and reactive sulfur compounds from anthropogenic and natural sources, which play a role in formation of aerosols and clouds. Secondly, in urban environments, emissions of reactive trace gases are precursors to, and components in, photochemical smog and fine particulate pollution or haze. Both of these can have adverse effects on human health, plants, and materials. Assessing the role and impacts of reactive gases in the atmosphere requires knowledge of the global distribution and long-term changes in their abundance. Observations of their background levels are also essential for understanding long-range pollution transport, which in turn is crucial for assessing the success of regional to local emission reduction activities.

Measurements of reactive gases are challenging. Their mole fractions are typically in the range of  $10^{-9}$  (i.e. nmol of gas per mol of air; in practice equivalent to mixing ratios of parts per billion or ppb) to  $10^{-12}$  (i.e. pmol/mol or parts per trillion = ppt). Therefore, sophisticated instrumentation is needed to quantify the abundance of reactive gases with known accuracy. Furthermore, reactive gases are often difficult to sample because of their reactivity. Maintaining consistent calibration over long periods can be challenging, because some of the reference materials may be unstable. The long-term trends of reactive gases are generally small relative to their atmospheric variability. Furthermore, their temporal changes in the troposphere can vary significantly among regions due to the inhomogeneity of natural and anthropogenic sources. The regional representativeness of measurements at individual stations may thus be limited. These complications significantly exacerbate the interpretation of trend analyses of trace gases.

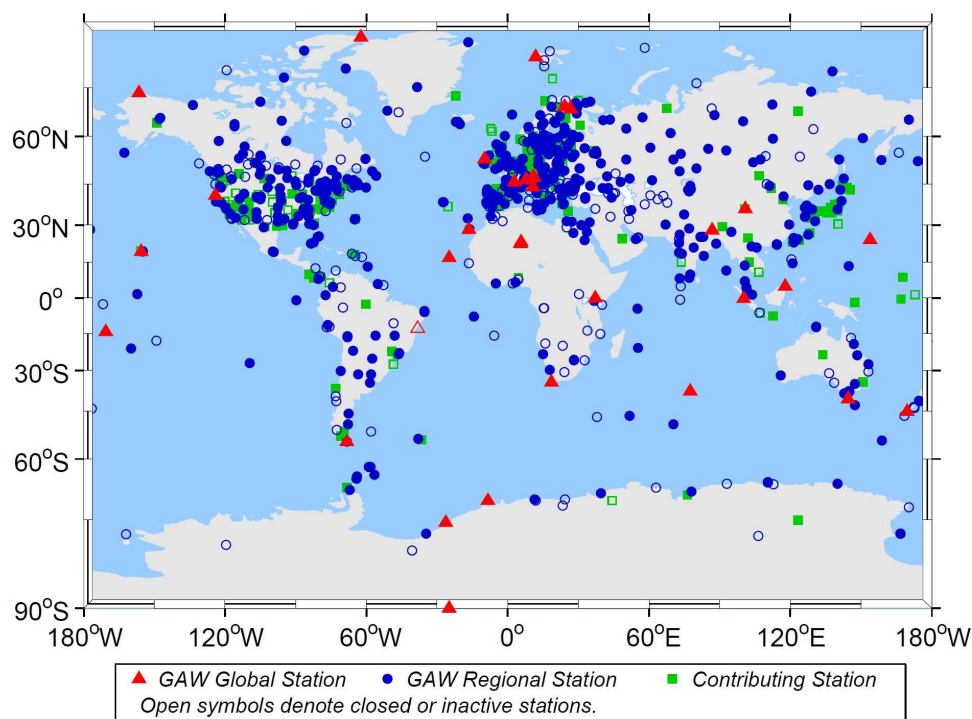
In the past, the duration of long-term observation programs for reactive gases were often limited because they were tied to the career of well trained and dedicated operators. Two examples of discontinued monitoring are the precipitation chemistry work of R. A. Smith in the UK in the 1850s–1870s (Smith, 1872), and the ozone measurements of A. Levy at Montsouris Observatory, Paris, France from 1876 to 1910 (Volz and Kley, 1988). Since 1989, the World Meteorological Organization (WMO) Global Atmosphere Watch (GAW) program provides a framework to support long-term consistent measurements of atmospheric constituents. The GAW framework constitutes: (a) a sound institutional base committed to long term measurements; (b) agreement on standard measurement techniques and procedures; (c) the provision of unambiguous, stable, and high-precision calibration methods and calibration standards; (d) guidelines for quality control and assurance, and (e) the provision for archiving and distributing the data for its ongoing use in atmospheric research. Measurements of atmospheric constituents are not performed by GAW itself, but are typically collaborative programs carried out by national hydro-meteorological services, research institutes, and universities.

Reactive gases are one of six focal areas in WMO/GAW. The others are stratospheric ozone, greenhouse gases, aerosols, precipitation chemistry (now renamed to total atmospheric deposition), and UV radiation. The focal areas are complemented by the GAW urban meteorology and environment (GURME) project, and two expert teams on World Data Centers and on Near-Real-Time Chemical Data Transfer. GAW seeks to “reduce environmental risks to society and meet the requirements of environmental conventions, strengthen capabilities to predict climate, weather and air quality, and contribute to scientific assessments in support of environmental policy through maintaining and applying global, long-term observations of the chemical composition and selected physical characteristics of the atmosphere, emphasizing quality assurance and quality control, [and] delivering integrated products and services of relevance to users.” (WMO, 2007a).

This article describes the surface-based observational network of reactive gases within GAW and its underpinning scientific and data management activities. While the strategy of GAW extends beyond surface observations and increasingly seeks their integration with airborne and satellite measurements, the program originated from the build-up of a global network of background stations, and these still remain the backbone and the unique feature of GAW.

Figure 1 presents an overview of the GAW network with respect to reactive gases. The network consists of “Global”, “Regional”, and “Contributing” stations. The designation of a station as “Global” or “Regional” depends primarily on the breadth of measurements performed (see [http://www.wmo.int/pages/prog/arep/gaw/join\\_GAW.html](http://www.wmo.int/pages/prog/arep/gaw/join_GAW.html)) and should not be interpreted as a label that would characterize the representativeness of the station's measurements. Although almost all “Global” stations are indeed far away from local pollution sources, this is also true for many “Regional” stations. In addition to the GAW “Global” and “Regional” stations, several stations with measurements organized under other national or regional programs also contribute to the GAW network of surface observations. All of the 30 “Global” stations and a large number of “Regional” stations measure at least some reactive gases, but there are many “Regional” stations (not depicted in Figure 1) which focus on other thematic areas (Table 1). Information about all stations in the GAW network can be obtained from the GAW Station Information System (GAWSIS; <http://gaw.empa.ch/gawsis/>).

Open access to GAW reactive gases data is provided through the World Data Center for Greenhouse Gases (WDCGG) hosted by the Japan Meteorological Agency in Tokyo (<http://ds.data.jma.go.jp/gmd/wdcgg/>). Some historical surface ozone observations can be found at the World Ozone and UV Data Center



**Figure 1**

The Global Atmosphere Watch network of reactive gases observations.

This map shows all stations measuring at least one reactive gas according to the GAW Station Information System (GAWSIS; <http://gaw.empa.ch/gawsis/>). Inactive stations or discontinued measurements are shown as open symbols. Note that the actual density of measurements varies by parameter, and that not all of the stations registered in GAWSIS regularly report data to the World Data Center for Greenhouse Gases (see Table 1).

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(WOUDC; <http://www.woudc.org>). Data from contributing networks normally are available from the programs' respective databases. The availability of such data through the GAW World Data Center may be limited.

This paper is structured as follows. Section 2 outlines the general quality assurance and control principles which are adhered to across the entire GAW program. Section 3 describes the reactive gases addressed by GAW activities, including: (a) motivation for observations with a brief summary of past changes, (b) recommended measurement methods and quality assurance practices, and (c) the existing network of observations in the GAW program. Section 4 discusses the current status of the GAW reactive gases data archive, and section 5 highlights some research applications of GAW reactive gases data. The paper ends with some concluding remarks and an outlook to the next phase of the GAW program (section 6).

The majority of the authors of this paper are current and previous members of the GAW Scientific Advisory Group on reactive gases (SAG RG), who are advising on priorities and implementation of activities of the program. Furthermore, they establish links between GAW and other regional and global monitoring and research networks, promote the use of GAW data and seek communication with data users. The GAW measurements and central facilities are supported by national funding from WMO member states and the program is managed by the WMO/GAW secretariat in Geneva.

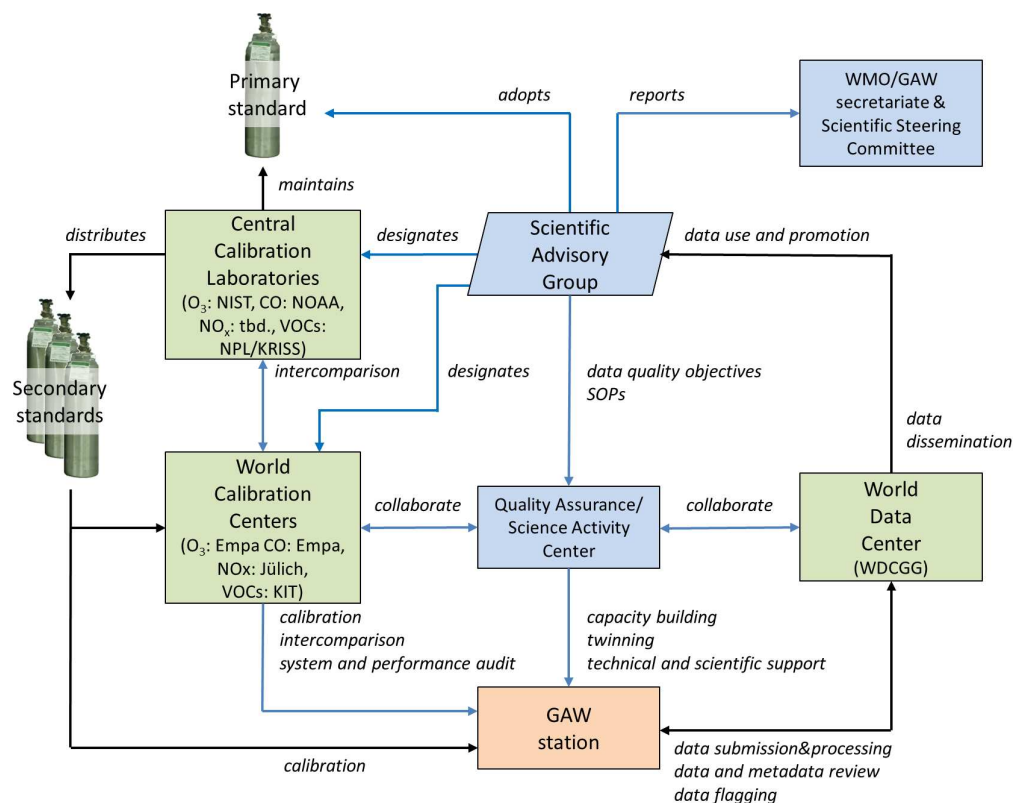
**Table 1.** Number of global and regional GAW stations measuring and reporting the various reactive gases substances

Substance	Global stations (total: 30)		Regional stations (total: 647)	
	Registered in GAWSIS	≥5 years of data in WDCGG archive	Registered in GAWSIS	≥5 years of data in WDCGG archive
Surface ozone	30	25	125	46
Carbon monoxide	29	23	88	62
NO <sub>x</sub> <sup>a</sup>	6	3	18	9
VOCs <sup>b</sup>	26	16	47	23
SO <sub>2</sub>	13	4	97	32

<sup>a</sup> Listed here are the number of sites with both NO and NO<sub>2</sub> data submissions. Twenty-five stations only submitted NO<sub>2</sub> data.

<sup>b</sup> In addition to the Global and Regional stations listed here, 84 sampling sites of the UCI flask network have been registered at the WDCGG as “mobile platforms” where between 1 and 595 samples were taken until 2014 (WMO, 2015).

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**Figure 2**

Overview of the GAW quality assurance and quality control system.

Diagram of central facilities for the quality assurance of reactive gases in GAW and their role in the quality assurance framework (after WMO/GAW 2007). SOP: standard operating procedures. Acronyms of specific institutions are explained in the text.

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## 2. The GAW quality management framework

High quality and long-term compatible time series of relevant atmospheric observations are an essential prerequisite to understand the dynamical, physical and chemical state of the atmosphere and its changes from seasonal to multi-decadal time scales. In order to achieve this goal, the WMO/GAW Program has put in place a dedicated quality management framework. The main principles of this are:

- Long-term continuity of observations;
- The definition of required quality of observations through data quality objectives (DQOs);
- Establishment of measurement techniques that allow meeting the quality targets through harmonized measurement guidelines and standard operating procedures;
- Network-wide use of one reference standard or scale (primary standard);
- Full traceability to the primary standard of all measurements made within the network;
- Complete and comprehensive documentation of meta information related to the measurements, operation, maintenance, and calibrations;
- Regular independent assessments (system and performance audits);
- Timely submission of data and associated metadata to the responsible World Data Center permitting independent review of data by a wider community;
- Training of station operators and the formation of partnerships between more and less experienced facilities (“twinning”).

The general quality assurance and quality control (QA/QC) concept is described in the WMO/GAW Strategic Plan 2008–2015 (WMO, 2007b) and its addendum (WMO, 2011b). A flow chart depicting the connections and interactions between the different entities is shown in Figure 2.

For each atmospheric constituent, data quality objectives are defined in the respective measurement guidelines (Table 2). These documents are written by members of the Scientific Advisory Group in consultation with other experts. They are regularly reviewed and updated. A requirement for comparability between observations from different sites is to have consistency of measurement protocols within the observing network.

Central facilities have been established within GAW in order to implement the quality management framework principles. Central Calibration Laboratories (CCLs) are responsible for long-term support of the network reference materials, i.e. they maintain the primary calibration standards. Often, the CCLs work in collaboration with the International Bureau of Weight and Measures (BIPM) in order to achieve consistency of standards beyond the field of atmospheric composition measurements. World Calibration Centers (WCCs) are assigned to conduct independent quality control audits and inter-comparison campaigns. They may also



Table 2. GAW reactive gases documents<sup>a</sup>

Compound	Measurement Guidelines GAW Report Number (reference)	Other Documents GAW Report Number (reference)
Ozone	209 (WMO, 2013)	ozone sondes: 201 (WMO, 2011d) ozone (data) workshop: 199 (WMO, 2011c)
CO	192 (WMO, 2010)	calibration scale: 206 <sup>b</sup> (WMO, 2014) network, QA/QC:166 <sup>b</sup> (WMO, 2006)
VOC	in preparation	general recommendations: 171 <sup>b</sup> (WMO, 2007a) sampling SOP: 204 (WMO, 2012)
NO/NO <sub>2</sub> /NO <sub>y</sub>	in preparation	general recommendations: 195 <sup>b</sup> (WMO, 2011a)
SO <sub>2</sub>	--	general recommendations: 143 <sup>c</sup> (WMO, 2001)
Strategic Plan 2008–2015: 172 (WMO, 2007b); Addendum 2012–2015: 197 (WMO, 2011b)		
Near real-time data delivery: 189 (WMO, 2010a)		
WDCGG data submission: 174 (WMO, 2008), 188 (WMO, 2009),		

<sup>a</sup>The numbers refer to the GAW report number (see <http://www.wmo.int/pages/prog/arep/gaw/gaw-reports.html>). These reports form an essential part of the GAW quality management framework.

<sup>b</sup>Workshop proceedings

<sup>c</sup>Global Atmosphere Watch Measurements Guide (WMO TD No. 1073)

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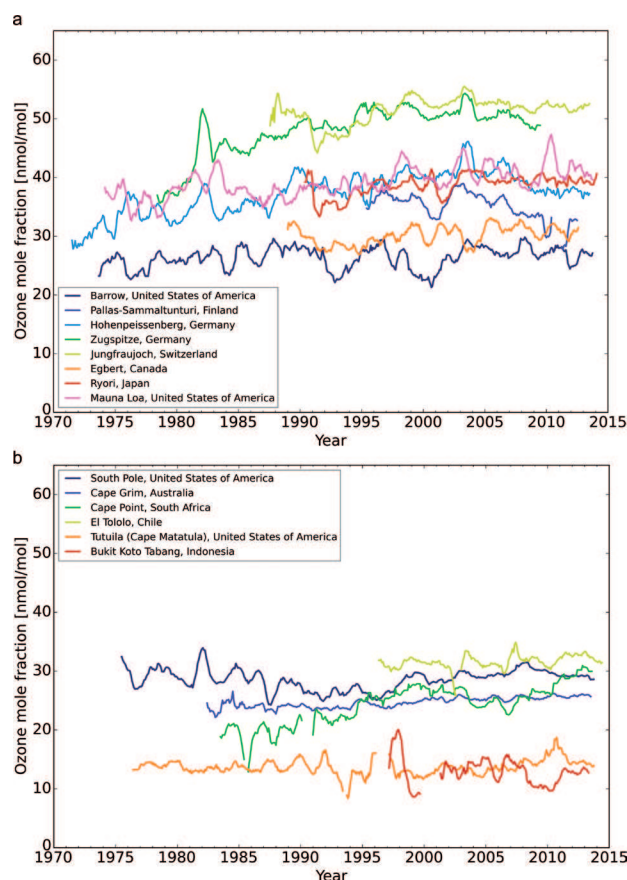
provide a link to the CCL reference if stations are unable to obtain the reference standard from the CCL directly. Each data provider is requested to maintain the link to the CCL reference as close as possible, to have the fewest possible number of intermediate standards between the primary standard and the station standard.

Central Calibration Laboratories have been established for ozone and monoterpenes at the National Institute of Standards and Technology (NIST, Gaithersburg, USA), CO at the National Oceanic and Atmospheric Administration (NOAA, Boulder, USA), and various non-methane volatile organic compounds (VOCs) at the National Physical Laboratory (NPL, Teddington, UK). CCLs for oxygenated VOCs and NO<sub>x</sub> are currently in the planning. World Calibration Centers exist for O<sub>3</sub> and CO at Empa, the Swiss Federal Laboratories for Materials Science and Technology, Switzerland, VOCs at the Karlsruhe Institute of Technology Institute of Meteorology and Climate Research/Atmospheric Environmental Research (KIT/IMK-IFU), Germany, and NO<sub>x</sub> at the Research Center Jülich, Germany. Examples of WCC quality assurance audits are shown in the sections on CO and VOCs below.

Timely data submission is an important aspect of quality management, because it allows for the data to be used and assessed by experts from the SAG RG and the scientific community. Submission of reactive gases data to the World Data Center for Greenhouse Gases in Japan is expected to occur within one year after measurement. Unfortunately, not all stations in the GAW network adhere to the principle of timely data submission. Therefore, the SAG RG is currently increasing their efforts to help the data providers to overcome difficulties with the data submission procedures. Staff at the Japanese Meteorological Agency support data submitters with data formatting, calculation of averages, and specification of metadata. Descriptive information on the station and the measured parameters should regularly be updated in GAWSIS

High quality observations can only be performed by well trained personnel. To address this dimension of quality assurance a dedicated training program for station personnel has been established. The GAW Training and Education Center (GAWTEC; <http://www.gawtec.de>) is based at the Environmental Research Station Schneefernerhaus in Germany. Dedicated 2-week technical training courses are held for GAW station operators, primarily targeting junior personnel from developing countries. Generally two training courses per year are given covering selected GAW thematic areas. The courses cover measurement techniques, lab courses, theoretical background of atmospheric physics and chemistry, and data handling and interpretation. The majority of the lecturers are experienced experts and scientists from the GAW community. Since GAWTEC was established in 2001 more than 280 persons from 58 countries have been trained. GAWTEC helps not only with knowledge transfer but also facilitates international networking between the operators of GAW stations.

Other elements of the GAW quality management framework are the Quality Assurance/Science Activity Centers (QA/SACs). These are being established to perform network-wide data quality and science-related functions. Some QA/SACs already provide technical and scientific support and training to ensure adequate data quality and they complement the SAG RG activities in promoting the scientific exploration of the data.



**Figure 3**

Time series of surface ozone mole fractions at selected GAW stations.

Hourly data from the WDCGG archive were averaged to monthly mean values, months with less than 67% coverage were excluded, and a 12-months running mean was applied with the condition that at least 8 months had valid data. Panel a shows ozone series from the Northern Hemisphere, and panel b shows data from the Southern Hemisphere.

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## 3. Reactive gases measurements in GAW

### 3.1 Ozone

Ozone in the troposphere is relevant to the human environment in several respects:

- As a strong oxidant, ozone has a direct impact on human respiratory health and impairs the growth of vegetation;
- It acts as a greenhouse gas with direct radiative forcing on the atmosphere;
- It is the primary source of the hydroxyl radical which controls the chemical lifetimes of many atmospheric gases;
- Ozone reduces photosynthetic activity of vegetation and thereby indirectly reduces CO<sub>2</sub> sequestration of the biosphere, which further amplifies its role in climate forcing;
- Tropospheric ozone contributes to filtering harmful solar ultraviolet radiation.

Ozone has no direct emission sources and is exclusively formed in the atmosphere as a result of photolytic decomposition of precursor molecules and subsequent chemical reactions. Its mole fraction in the background atmosphere ranges from less than 15 nmol mol<sup>-1</sup> in the tropical Pacific to some 50 nmol mol<sup>-1</sup> in the mid-latitudes of the Northern Hemisphere (Figure 3). Generally, mole fractions are larger in the Northern Hemisphere compared to the Southern Hemisphere, and they increase with altitude. The available surface ozone measurements indicate globally increasing mole fractions from the early 20<sup>th</sup> century until about the year 2000 (e.g. Cooper et al., 2014, and references therein). In the Northern Hemisphere, ozone mole fractions have almost doubled between 1950 and 2000. During the last decade most sites show either no trend or a slight downward trend in surface ozone mole fractions except for East Asia where mole fractions were mostly increasing. A more detailed discussion on ozone trends can be found in section 5.

The current recommended principle for measuring ozone is the UV absorption method. Prior to the commencement of GAW, surface ozone measurements were made using a variety of potassium iodide wet chemical and ethylene chemiluminescence ozone analyzers. It is desirable that these records be incorporated into current analyses, and often this is done. However, potential differences between the UV absorption method and earlier methods are not well characterized. The absence of comparisons between older and more modern surface ozone measurement techniques is a substantial limitation to reliably reproduce multi-decadal trends in tropospheric ozone.

**Table 3. Timeline for some key events in background ozone monitoring**

1960	World Ozone Data Center commenced, has provision for submitting surface ozone data, but stratospheric ozone is the main focus.
1971	WMO commences the Background Air Pollution Monitoring Network (BAPMoN)
1972	Ultraviolet ozone continuous monitor first reported in literature
1983	NBS (now NIST) produces the standard reference photometer for ozone
1984	International Ozone Commission adopts the Hearn (1961) absorption cross-section at 253.65 nm.
1989	BAPMoN and Global Ozone Observing System (GO <sub>2</sub> OS) merged to form GAW
1990	World Data Center on Greenhouse Gases (WDCGG) commences operation
1994	GAW Tropospheric Ozone guidelines (GAW Report No 97)
1996	World Calibration Center (WCC-Empa) for Surface Ozone established
2013	Revised GAW Tropospheric Ozone guidelines (GAW Report No 209)
2014	Evidence from studies at the Bureau International des Poids et Mesures (BIPM), France, University of Bremen, Germany, and the National Institute for Environmental Studies (NIES), Japan, indicate accepted value of the ozone absorption cross-section at 253.65 nm should be reduced by approximately 2%.

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Some key events in the development of GAW surface ozone observations are recorded in Table 3. Guidelines for the measurement of ozone at GAW sites were developed in the GAW report no. 97 (WMO, 1994) and revised and expanded in the GAW report no. 209 (WMO, 2013). The Standard Reference Photometer at NIST has been adopted as the primary standard for the network (see section 2). The WCC for ozone has conducted 78 site audits in the GAW network since 1996. Audit results up to 2008 were reported by Buchmann et al. (2009). A comprehensive analysis of the consistency of long-term ozone records is under way in the Tropospheric Ozone Assessment Report (TOAR; <http://www.igacproject.org/TOAR>) initiative.

Because ozone cannot be stored without decomposition, the standard for ozone measurements is its absorption cross-section at 253.65 nm. This absorption cross-section was determined by Hearn (1961) and adopted by the International Ozone Commission (IOC) in 1984. Subsequent studies supported the results (e.g. Viallon et al., 2006). Recently, two independent groups have produced new data on ozone absorption cross-sections (Gorshlev et al., 2014; Viallon et al., 2015). Application of these new data will increase the reported tropospheric ozone mole fractions by approximately 2%. The change will have implications for global radiative forcing estimates and air quality regulations. This illustrates the importance of ongoing development of accurate primary standards for the GAW program.

Substantial gaps exist in the coverage of global surface ozone observations. Out of the 71 stations having a surface ozone record of at least 5 years in the WDCGG archive (Table 1; for details on the data availability see section 4), only 19 are located in the Southern Hemisphere, and large regions of the world remain with no observations at all. Many more observations than those included in Table 1 exist from various regional networks (for example the US Clean Air Status and Trends Network, CASTNET, the US National Park Service, the European Monitoring and Evaluation Programme, EMEP, or the Acid Deposition Monitoring Network in East Asia, EANET). “Background” stations, i.e. stations with little or no direct pollution impacts, are also included in some national or regional air pollution monitoring networks such as the Canadian Air and Precipitation Monitoring Network (CAPMoN). Nevertheless, in many world regions, observations made specifically for the GAW program are the only available surface ozone measurements, and these measurements would often not be possible without support from GAW partners.

### 3.2 Carbon monoxide

Carbon monoxide (CO) has been a key species within the GAW reactive gases program from its inception, since it is a by-product from many atmospheric reactions and a primary tracer of combustion of carbonaceous fuels. The reaction of CO with the hydroxyl radical (OH) is the dominant sink for OH. Together with nitrogen oxides CO largely controls the overall oxidative capacity of the atmosphere (Logan et al., 1981). It also contributes indirectly to radiative forcing (Daniel and Solomon, 1998). With a lifetime ranging from 10 days to more than a year, depending on the season and the geographic location, CO is also an excellent tracer of atmospheric transport. Its primary sources, i.e. direct emissions from the combustion of fossil fuels and biomass, and the oxidation of methane and VOCs, are relatively well known (Logan et al., 1981; Holloway et al., 2000; Monks et al., 2009; Granier et al., 2011).

Typical atmospheric mole fractions of CO range from 30 to 300 nmol mol<sup>-1</sup>, with southern hemispheric values generally lower than northern hemispheric values. Anthropogenic emissions in the mid to high northern latitudes lead to increasing concentrations through early spring. The summertime seasonal minimum is largely driven by the seasonal maximum in the OH mixing ratio. A reasonable coverage of continuous



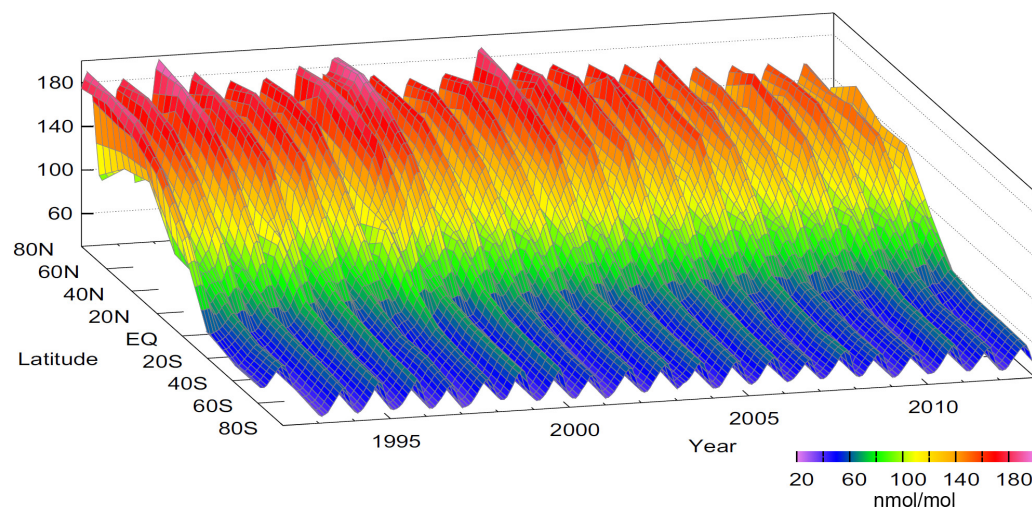


Figure 4

Latitude-Time diagram of carbon monoxide mole fractions from selected GAW sites.

This figure has been adapted from WMO (2015). For details on the data selection procedure, see WMO (2015).

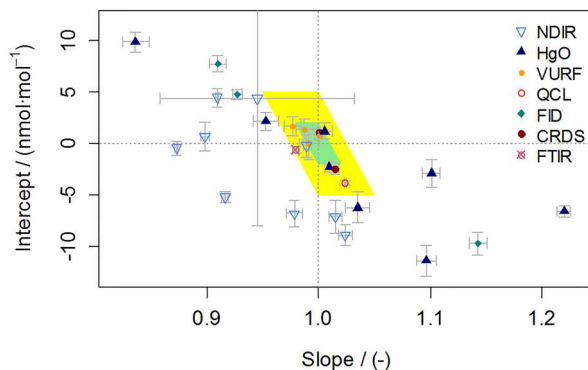
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CO observations is available since the mid-1990s (Table 1), although similar data gaps exist as for surface ozone. CO measurements at GAW stations provide very good coverage in the Northern Hemisphere where continental and global scale programs are established in the USA/Canada, Western Europe and China. Laboratories in the Southern Hemisphere collaborate with partners from the Northern Hemisphere to maintain measurement programs to define CO distributions in the Southern Hemisphere. However, measurements in the tropics are generally under represented. Additional measurements are needed to better constrain CO emissions from biofuel and biomass burning, and from oxidation of VOCs.

Before 1990 a limited number of measurements suggested an increasing atmospheric concentration. Over the past 25 years measurements made by GAW partners have shown a significant decrease in the Northern Hemisphere (Figure 4; Novelli et al., 1994, 2003; Isaksen et al., 2009; Zellweger et al., 2009; WMO, 2015), while CO trends in the Southern Hemisphere, if any, are smaller and difficult to quantify. Modeling studies, which often make use of GAW observations, indicate that the decrease is primarily due to emissions controls enacted in the mid-1970s. CO mole fractions feature a strong year to year variability driven by the extent of biomass burning (Langenfelds et al., 2002; Novelli et al., 2003; Simmonds et al., 2005; Schultz et al., 2008), which complicates the detection of trends (Strode and Pawson, 2013).

An overview of the history and performance of different CO measurement techniques is given in the GAW report no. 192 (WMO, 2010b). Before the early 2000s atmospheric measurements were typically made using gas chromatography with either hot mercuric oxide detection (GC-HgO), or flame ionization detection (FID) using a methanizer, or by non-dispersive infrared detection (NDIR). The GC-HgO typically gives a non-linear response and requires a set of calibration standards that cover a large range of ambient levels. However, these standards are often subject to drift and difficult to maintain over time (see below). NDIR instruments require relatively long averaging times to achieve sufficient repeatability, and their high detection limits are a limiting factor for measurements under very clean conditions, i.e. in the Southern Hemisphere. Nevertheless, this method is attractive for observations from aircraft because of the demonstrated long-term stability and because it requires no high-pressure calibration gas cylinders. In the Measurement of Ozone and Water Vapour on Airbus in-service Aircraft (MOZAIC; Marenco et al., 1998) and In-service Aircraft for a Global Observing System (IAGOS; Petzold et al., 2015) programs, improved versions of commercial NDIR instruments are employed which can measure CO down to mole fractions below 25 nmol mol<sup>-1</sup> (Nédélec et al., 2015). More recently, several new methods and instruments have become available which appear to be better suited for measuring atmospheric CO (Zellweger et al., 2012). These techniques include Vacuum UV Resonance Fluorescence (VURF) (Gerbig et al., 1999), Cavity Ring Down Spectroscopy (CRDS) (Baer et al., 2002; Chen et al., 2013), Quantum Cascade Laser Spectroscopy (QCL) (Morgan et al., 2015), and Fourier Transform Infrared Spectroscopy (FTIR) (Hammer et al., 2013).

The WMO/GAW scale for atmospheric measurements of CO is maintained by the CCL at NOAA (WMO, 2010b). The scale is defined by several sets of primary standards, their assigned mole fractions and their analysis. CO primary standards are prepared by a gravimetric method with new sets made every 4–6 years. Stability of the scale is evaluated through the long-term calibration of a suite of surveillance cylinders. Revision of previous scales was deemed necessary as new primary standards and improved analytical methods led to a significantly different interpretation of previous measurement results. The current scale, identified as WMO X2014 CO, covers the period from 1993 to present. It will replace the previous WMO X2000 and X2004 scales when fully implemented in 2015 (for more information go to <http://www.esrl.noaa.gov/ccl/co-scale.html>).



The compatibility of CO measurements made at GAW stations has been evaluated through co-located sampling (Masarie et al., 2001), informal comparison of measurements organized by the CCL and WCC, and on-site audits. An overview of the WCC quality assurance of CO is given in Buchmann et al. (2009). Figure 5 shows the network compatibility for carbon monoxide measurements using data from 29 audits from 2008 to 2014. Calibration results from the WCC travel standards are plotted against results obtained from GAW partner stations using different types of analyzers. For measurements traceable to a common reference, the intercept/slope pairs are expected to be homogeneously distributed around an intercept of 0 and a slope of 1. It is clear that the comparability goal of  $2 \text{ nmol mol}^{-1}$  for the range of 0 to  $200 \text{ nmol mol}^{-1}$  CO is met only in a few cases, and also the extended comparability goal of  $5 \text{ nmol mol}^{-1}$  is often exceeded for measurements made with non-dispersive infrared spectroscopy and gas chromatography. In contrast, most of the comparisons involving newer measurement techniques meet at least the extended comparability goal. The quality of CO measurements in GAW is therefore expected to improve when older instruments are replaced with new technologies at the stations.

### 3.3 Non-methane volatile organic compounds

A wide range of non-methane volatile organic compounds (VOCs) are present in the background atmosphere. These include simple short chain alkanes such as ethane and propane, the more complex unsaturated and aromatic compounds, those with an oxygen functionality such as alcohols, aldehydes and ketones, and organo-sulfur and organo-nitrogen compounds. A list of individual gases that have been considered within the GAW program is given in Table 4. The significance of VOCs in the background atmosphere is associated with their oxidation products which promote the formation of ozone, CO, and aerosol and can be oxidized to organic acids which contribute to atmospheric acidity. Atmospheric mole fractions span many orders of magnitude with upper levels in the  $\text{nmol mol}^{-1}$  range (even  $\mu\text{mol mol}^{-1}$  levels have been measured under highly polluted conditions).

Emissions from vegetation constitute the largest source of VOCs globally. Compounds emitted from the terrestrial and marine biosphere include isoprene, monoterpenes, small alkenes, methanol and other oxygenates, and others. VOCs are also released from a wide array of anthropogenic processes, such as combustion, industrial and domestic solvents, fuel evaporation, and oil and gas extraction activities. The lifetimes of VOCs in the atmosphere vary significantly between individual species. For instance, ethane has a lifetime between 2 and 6 months depending on the season, and isoprene has a lifetime of only ~30 minutes. The primary sinks of VOCs are oxidation *via* the hydroxyl radical, and *via* ozone, with other minor loss routes through reaction with nitrate and chlorine radicals.

In the 1980s various academic research groups investigated the distribution and seasonality of VOCs in the remote atmosphere and compiled the first global estimates of VOC sources and sinks. Measurements were mostly campaign-based and covered the marine and continental atmosphere, seasonal cycles, and vertical profiles (for example Rudolph and Ehhalt, 1981; Singh and Salas, 1982; Greenberg and Zimmerman, 1984; Bonsang and Lambert, 1985; Blake et al., 1992; Kopppmann et al., 1990; Rudolph et al., 1992a). The first long-term observations were reported by Blake and Rowland (1986), Hov et al. (1988), and Rudolph et al. (1992b). In the late 1980s and 1990s efforts to monitor VOCs in the atmosphere were increased as environmental policies in Europe (EMEP, 1990) and the US demanded effective strategies to improve air quality in cities and surrounding areas. Several research initiatives were launched in North America and Europe to monitor VOCs, for example the Tropospheric Ozone Project (TOR) in Europe (e.g. Klemp et al., 1997). The Environmental Protection Agency in the USA established their Air Quality System including VOCs observations in the early 1990s (<http://www.epa.gov/ttn/airs/airsaqs/>). In the late 1990s the atmospheric sciences community suggested combining the different observational capacities in GAW to facilitate data access

**Figure 5**

Results of CO audits conducted by WCC-Empa between 2008 and 2014.

Shown are the slopes (x axis) and intercepts (y axis) of the linear regression between the stations' calibration measurements and the Empa reference standard. The green and yellow areas cover the range of slope-intercept combinations for a maximum bias of  $2 \text{ nmol mol}^{-1}$  (WMO/GAW compatibility goal) and  $5 \text{ nmol mol}^{-1}$  (extended compatibility goal) for the mole fraction range of  $50\text{--}200 \text{ nmol mol}^{-1}$  CO. The different measurement techniques employed were: NDIR: non-dispersive infrared detection, HgO: gas chromatography with hot mercuric oxide detector, VURF: Vacuum UV Resonance Fluorescence, QCL: Quantum Cascade Laser Spectroscopy, FID: gas chromatography with flame ionization detector, CRDS: Cavity Ring Down Spectroscopy, FTIR: Fourier Transform Infrared Spectroscopy.

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**Table 4. Volatile organic compounds measured within the GAW reactive gases program with mid-summer lifetime estimate, scientific interests and significance, analysis method, and network type**

Molecule	Lifetime (T=298 K and [OH]=10 <sup>6</sup> cm <sup>-3</sup> )	Importance to GAW	Analysis Method <sup>a</sup>	Network Type
Ethane	1.5 months	Natural sources, biomass burning, fossil fuel, ocean production, trend in size of seasonal cycle, research on methane sources	GC/FID	Global
Propane	11 days	Natural sources, biomass burning, fossil fuel, ocean production, research on methane sources	GC/FID	Global
Acetylene	15 days	Motor vehicle tracer, biomass burning tracer, ratios to the other hydrocarbons/age of plume air, trends	GC/FID	Global
Isoprene	3 hours	Mostly biosphere product, sensitive to temperature/land use/climate change, O <sub>3</sub> precursor, precursor to formaldehyde	GC/FID, PTR-MS	Mid latitudes and tropics
Formaldehyde	1 day	Indicator of isoprene oxidation, biomass burning, comparison with satellites, trends	DOAS	Small number of sites in tropics for comparison with satellites
Monoterpenes	1.5 hours	Mostly biosphere product, sensitive to temperature/land use/climate change, precursors to organic aerosols	GC/MS, PTR-MS	Selected sites in forested areas
Acetonitrile	0.5–1 year	Biomass burning indicator, biofuel burning indicator	GC/MS, PTR-MS	Global
Methanol	12 days	Sources in the biosphere (methane oxidation), abundant oxidation product	GC/FID, PTR-MS	Global
Ethanol	4 days	Tracer of alternative fuel usage	GC/FID, PTR-MS	Global
Acetone	1.7 months	Abundant oxidation product, free radical source in the upper troposphere	GC/FID, PTR-MS	Global
DMS	2 days	Major natural sulphur source, sulphate aerosol precursor, tracer of marine bioproductivity	GC/FID, PTR-MS	Global Marine
Benzene	10 days	Tracer of combustion, biomass burning indicator	GC/FID, GC-MS	Global
Toluene	2 days	Ratio to benzene used for air mass age, precursor to particulates	GC/FID, GC-MS	Global
Iso/n-Butane	5 days	Chemical processing indicator, source attribution, ozone production, Indication of halogen chemistry	GC/FID, GC-MS	Global
Iso/n-Pentane	3 days	Ratio provides impact of NO <sub>3</sub> chemistry, indication of halogen chemistry, source attribution	GC/FID, GC-MS	Global

<sup>a</sup> GC/FID: Gas Chromatography - Flame Ionization Detection; GC/MS: Gas Chromatography - Mass Spectrometry; DOAS: Different Optical Absorption Spectrometry; PTR-MS: Proton Transfer Reaction-Mass Spectrometry

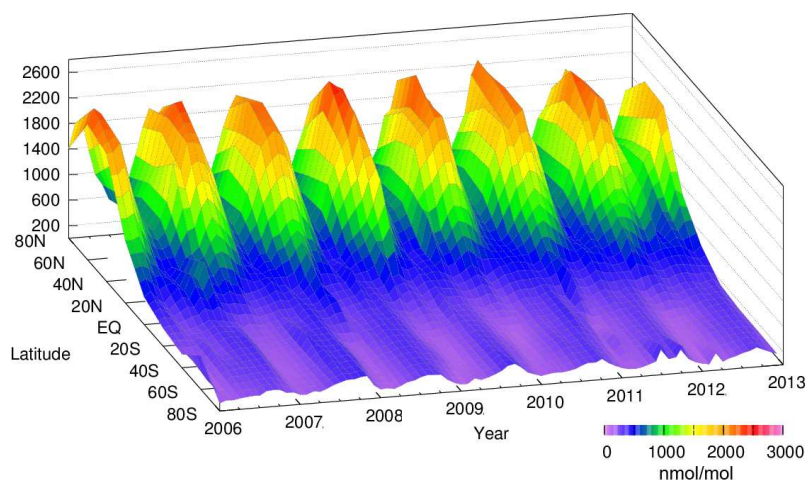
doi: 10.12952/journal.elementa.000067.t004

and improve data quality. At least three flask networks have been established since then. At these network stations or mobile platforms whole air samples are collected more or less regularly into either stainless steel or glass flasks. These samples are then shipped to a central analytical laboratory for analysis.

For roughly 30% of the target VOCs listed in Table 4, global observations are now available. Notably, however, there are some key atmospheric species such as isoprene, monoterpenes, and methanol, for which there are few sustained observations. The value of global coverage can be seen in Figure 6, where GAW ethane data were plotted against time and latitude, yielding a mole fraction ‘surface’ that visually depicts the seasonal cycle and latitudinal gradient of ethane worldwide. This figure illustrates the strong enhancements of ethane in the Northern Hemisphere compared to the Southern Hemisphere, driven by enhanced emissions in the former. The current VOC network contributing to GAW comprises:

- A global distribution of observations derived from weekly flask sampling where the VOC measured are limited to the simple short chain hydrocarbons. This VOC monitoring builds on the NOAA Global Greenhouse Gas Reference Network and began in 2005 ([http://instaar.colorado.edu/ar1/Global\\_VOC.html](http://instaar.colorado.edu/ar1/Global_VOC.html); Pollmann et al., 2008);



**Figure 6**

Latitude-Time diagram of ethane mole fractions measured at selected GAW sites.

This figure has been adapted from WMO (2015). For details on the data selection procedure, see WMO (2015).

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- Long-term observations since 1996, four-times a year in different seasons from a north-south transect of sites in the Pacific and Americas area (University of California; Simpson et al., 2012);
- Contributed data from the European EMEP network (since the early 1990s; Tørseth et al., 2012);
- Continuous *in situ* observations made at the GAW stations Hohenpeissenberg (Germany; Plass-Dülmer et al., 2002; von Schneidemesser et al., 2010), Summit (Greenland; Helmig et al., 2015), Pico Mountain (Portugal; Helmig et al., 2008, 2015), Rigi and Jungfraujoch (Switzerland; Lanz et al., 2009), and Cape Verde (Republic of Cabo Verde; Read et al., 2009).

Trend analyses of available data sets including samples from firn and ice core records have shown a decline of VOCs in the background atmosphere over the past two decades (Von Schneidemesser et al., 2010; Aydin et al., 2011; Simpson et al., 2012; Worton et al., 2012; Helmig et al., 2014; 2015). VOC trends in Europe are less conclusive (Tørseth et al., 2012) because of large scatter in the data. Significant changes could only be detected for certain components and at specific stations. Where mole fractions are decreasing this is likely due to a decline in anthropogenic emissions due to reductions in solvent usage and improved vehicle exhaust gas controls. More details on the GAW VOC activities and findings from the data are presented by Helmig et al. (manuscript in preparation for this special issue).

The long-term measurement of atmospheric VOCs in cleaner environments requires their pre-concentration followed by gas chromatography. A wide selection of chromatography columns has been in use (Helmig, 1999). While earlier techniques relied on cryogenic focusing methods there has been a move towards solid adsorbent based enrichment methods since the mid-1990s. Detection and quantification is most commonly achieved by flame ionization detection (FID), which exhibits stable long-term response characteristics. Challenges arise from interferences of other primary air constituents in the sample air, including water vapor, ozone, and carbon dioxide. These must be removed in order to achieve an accurate VOC determination (Helmig, 1997; Plass-Dülmer et al., 2002). While new methods for VOC monitoring based on optical measurement and mass spectrometry (e.g. Proton-Transfer Mass Spectrometry; PTR-MS) have emerged during the last 15 years, GC-FID remains the dominant method in routine VOC observations, because of its stability and relatively low maintenance cost.

The WMO/GAW activities associated with VOCs have been refined through five expert workshops between 1995 and 2014. These workshops produced measurement protocol recommendations for VOCs that balance scientific interest with compatibility for long-term monitoring (e.g. WMO, 2007a, 2012). In 2014, a series of DQOs and requirements for calibration standards were developed based on user requirements for trend analysis, process studies, health effect studies, and model evaluation (ACTRIS, 2014). Recommendations for measurement procedures and technologies are under development.

Earlier inter-comparison experiments had identified the non-consistency of standards used for calibration of the analytical instruments as one of the major reasons for lacking data compatibility (Rappenglück et al., 2006). Therefore, a formal framework for VOC data quality assurance was developed (WMO, 2007a). CCLs were established at various National Metrological Institutes, each hosting the primary standards for a different group of VOCs. Primary standards are synthetic mixtures of VOCs in the  $\mu\text{mol mol}^{-1}$  range prepared in nitrogen. However, because these standards lack critical interfering gases, such as water vapor, ozone, and carbon dioxide, additional calibration measurements with whole air standards and in-situ inter-comparisons are also necessary (e.g. Apel et al., 2003; Plass-Dülmer et al., 2006; Hoerger et al., 2015). The WCC in Garmisch-Partenkirchen, Germany, has conducted 23 audits of VOC measurements since 2003 (Steinbrecher et al., manuscript in preparation for this special issue). GAW network compatibility for various VOCs is shown in Figure 7 (Weiss et al., 2013). For most of the audited laboratories the reported mole fractions of tested VOCs were within the specified GAW data quality objectives.

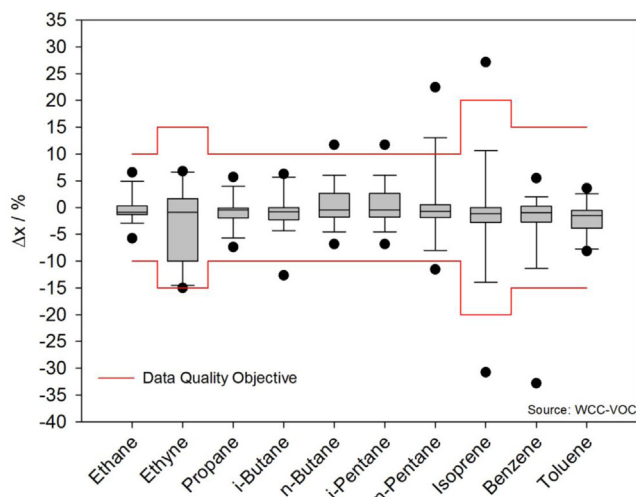


Figure 7

GAW network compatibility for target VOCs.

The box-plots show the statistical distribution of the percent deviation between station results and the value of the certified standard from 16 audits performed at 12 facilities around the globe since 2007. The boundaries of the boxes indicate the 25<sup>th</sup> and 75<sup>th</sup> percentiles. The horizontal lines within the boxes mark the medians, whiskers (error bars) above and below the boxes indicate the 10<sup>th</sup> and 90<sup>th</sup> percentiles. The black dots show the extreme deviations. The red line represents the GAW data quality objectives for network compatibility (WMO, 2007a).

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As with all other reactive gases there is a need to strengthen observational efforts and increase coverage, quality, and documentation of the observations. In Europe these issues are currently addressed through the Aerosols, Clouds, and Trace gases Research InfraStructure Network (ACTRIS) project. Measurement uncertainties associated with oxygenated VOC species (OVOCs), and protocols for determining and tracking the quality of OVOC and terpene measurements are needed. For oxygenated VOCs, dimethylsulfide, and acetonitrile there are as yet no common scales and there have been few comparisons of measurements. Also, measurement guidelines for emerging measurement techniques (PTR-MS, and laser optical methods) will need to be developed.

### 3.4 Nitrogen oxides

Nitrogen oxides play an important role in controlling the concentration of tropospheric ozone and hydroxyl radicals. They are engaged in fast chemical reaction cycles during daytime and they form key ingredients of nighttime chemistry in the planetary boundary layer. Nitrogen oxides can be oxidized to acidic species, forming acidic aerosol and precipitation. Some nitrogen oxides (e.g.  $\text{NO}_3$ ,  $\text{N}_2\text{O}_5$ ,  $\text{N}_2\text{O}_3$ ,  $\text{HNO}_2$ ,  $\text{HNO}_3$ ) are highly soluble and can easily be deposited, thus impacting ecosystems either beneficially by enhancing nutrients or detrimentally through acidification and eutrophication (Townsend and Howarth, 2010). Nitrogen oxides are also involved in reactions with organic molecules, where they can influence the reactivity and hence lifetime of VOC reaction products. Various organic nitrates, most notably peroxyacetyl nitrate (PAN), also act as reservoir species for reactive nitrogen oxides, thus enabling impacts of their emissions on regions remote from their emissions (Singh et al., 1986; Rudolph et al., 1987; Fischer et al., 2014).

$\text{NO}_x$  (i.e. the sum of nitric oxide NO and nitrogen dioxide  $\text{NO}_2$ ) is primarily emitted from high temperature combustion of fossil fuels in electricity generation and petroleum based motor vehicles, ships, aircraft etc. Lower temperature combustion of biomass in wildfires, deforestation, domestic burning etc. is another large group of sources. There are also natural sources from soils, plants, and by photochemical activation from nitrate in snow (Galbally and Roy, 1978; Davidson and Kingler, 1997; Honrath et al., 2000; Jones et al., 2001). In the upper troposphere, lightning constitutes an important source of  $\text{NO}_x$  (e.g. Schumann and Huntrieser, 2007; Martin et al., 2007), together with aircraft emissions (Köhler et al., 2013). While large areas of Europe and North America have seen a decrease in  $\text{NO}_x$  emissions during the past two decades and a corresponding decrease in atmospheric  $\text{NO}_x$  mole fractions (Tørseth et al., 2012; Zhou et al., 2013; Schneider et al., 2015), trends of  $\text{NO}_x$  mole fractions in other world regions (Asia and Africa) are positive due to the rapid increase of traffic and industrial development (Zhang et al. 2007; Schneider et al., 2015).

The mole fractions of NO and  $\text{NO}_2$  observed in the atmosphere depend very much on proximity to sources. Mole fractions up to 100's of  $\text{nmol mol}^{-1}$  can be detected in atmospheric plumes from fires, power stations and internal combustion sources. In the rural atmosphere NO and  $\text{NO}_2$  occur in mole fractions varying from a few tenths  $\text{nmol mol}^{-1}$  to  $\sim 10 \text{ nmol mol}^{-1}$ , with NO being present in daytime but practically absent at night. In the pristine atmosphere NO and  $\text{NO}_2$  mole fractions occur in the range  $1\text{--}50 \text{ pmol mol}^{-1}$  with the lower limit being the detection limit of current measurement systems (Carroll et al., 1990; Carpenter et al., 1997; Bradshaw et al., 1999; Galbally et al., 2000; Lee et al., 2009).

The recommended technique for measuring  $\text{NO}_x$  is chemiluminescence detection of NO *via* reaction with ozone.  $\text{NO}_2$  must be converted to NO in order to be measured. This is done with photolytic converters using either a xenon or methyl halide lamp, or blue light emitting diodes. Another widely used technique employing a heated molybdenum converter to reduce the  $\text{NO}_2$  to NO is no longer recommended, since other reactive nitrogen species are also partly converted to NO, leading to an overestimation of  $\text{NO}_x$  (Steinbacher



et al., 2007). More recently, direct measurement techniques for the detection of  $\text{NO}_2$ , including quantum cascade laser based absorption spectrometry (QCL; Tuzson et al., 2013), Cavity Attenuated Phase Shift Spectroscopy (CAPS; Kebabian et al., 2005), and Cavity Ringdown Spectroscopy (CRDS; Fuchs et al., 2009) have become available. While QCL is currently too difficult to operate in routine measurements, the latter measurement techniques are already appropriate for urban and continental background measurements, but further developments are needed if they shall be used in the remote pristine atmosphere (Wagner et al., 2011).

Within the GAW reactive gases program the focus is currently placed on the observations and analysis of the reactive nitrogen oxides  $\text{NO}$  and  $\text{NO}_2$ . It is foreseen that with development of specific measurement techniques this scope is to be extended to cover other nitrogen compounds (including PAN,  $\text{HNO}_3$  and alkyl nitrates) involved in the nitrogen cycle. Existing technologies to measure  $\text{NO}_y$  (i.e. the sum of all oxidized nitrogen compounds with oxidation number higher than one) are affected by uncertainties of calibration, interferences by other substances (e.g. HCN), and unstable conversion efficiencies. Hence, they appear less promising at this time.

GAW organized one  $\text{NO}_x$  expert workshop at Hohenpeissenberg, Germany in 2009, documented in the GAW Report 195 (WMO, 2011a). The meeting led to agreement on DQOs and recommendations concerning measuring techniques. The ACTRIS project collaborates with GAW on quality assurance issues of  $\text{NO}_x$ . In this context measurement guidelines and calibration procedures have been developed. Additionally, a round-robin-exercise and a side-by-side comparison have been performed. Both exercises showed that the DQOs can be achieved with commercial instruments if calibration and maintenance are properly performed. These exercises were thus important in putting European nitrogen oxide measurements on a homogenous, high quality level, and their outcomes will help to ensure network-wide quality standards if the number of  $\text{NO}_x$  measurement stations can be increased in the future. A specific challenge that has not been addressed by these activities is the reliable measurement of  $\text{NO}_x$  in the remote pristine atmosphere with mole fractions down to  $1 \text{ pmol mol}^{-1}$ .

The World Calibration Center for nitrogen oxides was established at the Forschungszentrum Jülich, Germany, in 2014, and a first site audit was performed at Hohenpeissenberg. It is foreseen that the National Physical Laboratory (NPL, Teddington, UK) will serve as the Central Calibration Laboratory (CCL) for  $\text{NO}$  and  $\text{NO}_2$ . While  $\text{NO}$  standard gases in cylinders meet the quality requirements related to accuracy and long term stability, there are some issues with the stability of  $\text{NO}_2$  in cylinders. Therefore, GAW recommends the use of  $\text{NO}$  standard gases and gas phase titration with ozone for calibration of  $\text{NO}_2$  measurements.

One important task for the GAW community is to foster measurement activities for nitrogen oxides outside Europe. There is good coverage of nitrogen oxides from GAW stations in Europe but almost complete absence of measurements for the rest of the world (WMO, 2015). This is partly due to the fact that instruments required for  $\text{NO}_x$  measurements in the pristine environment were only capable of campaign style operation until about a decade ago.

### 3.5 Sulfur dioxide ( $\text{SO}_2$ )

Sulphur dioxide ( $\text{SO}_2$ ) was measured in regional air quality networks and at several background sites in Europe and North America during the 1980s and 1990s when acid deposition was a major environmental problem in these regions. Due to rigorous emission reduction acid rain formation by  $\text{SO}_2$  is no longer a major concern in Europe and North America. However, it is still a serious issue in other parts of the world, e.g. Asia.

There are other scientific and air quality issues justifying a renewed interest to better understand the global sulphur cycle.  $\text{SO}_2$  is the precursor of sulphate aerosol, which contributes to ambient particulate matter levels and efficiently scatters radiation, thus impacting climate. Moreover, due to its emission signature (the sources are primarily industrial processes, energy production, and volcanic eruptions), and because of its atmospheric lifetime comparable to tropospheric ozone, it is a good tracer for evaluation of air mass origin. For these reasons it was decided to maintain and strengthen the efforts to measure  $\text{SO}_2$  within the GAW program. The first activities to establish a global  $\text{SO}_2$  network and develop measurement guidelines and calibration procedures have begun and shall be developed in the coming years in coordination with the GAW thematic groups on aerosols and total atmospheric deposition.

### 3.6 Other trace gases

Recognizing that there are many more species of interest to tropospheric chemistry than those measured within GAW, the Scientific Advisory Group has discussed if and how the list of substances could and should be expanded. The key criteria are to identify those compounds that are closely linked to atmospheric chemistry, whose monitoring would give important currently unavailable information on regional and global atmospheric changes, and that are suitable for observation in the GAW context.

Most of the key radicals that drive tropospheric chemistry,  $\text{OH}$ ,  $\text{HO}_2$ ,  $\text{NO}_3$ ,  $\text{Cl}$ ,  $\text{Br}$ ,  $\text{BrO}$ ,  $\text{I}$ , and  $\text{IO}$ , do not yet have stable and reliable measurement techniques and traceable standards for observation in the GAW context, although Berresheim et al. (2000) demonstrated the feasibility of long-term  $\text{OH}$  measurements at

the Hohenpeissenberg station. However, there are other substances that are closely linked to atmospheric chemistry and that would give important information on regional and global atmospheric changes, which are more suitable for monitoring at GAW stations. Under consideration are compounds that would complement  $\text{NO}_x$  or  $\text{SO}_2$  with respect to the nitrogen and sulfur cycles, and which could offer deeper insights into tropospheric radical oxidation chemistry. Potential candidates that will be further examined include additional nitrogen oxide compounds such as peroxyacetylnitrate (PAN),  $\text{NH}_3$ , amines,  $\text{H}_2\text{O}_2$ ,  $\text{CH}_3\text{OOH}$ , glyoxal and methyl glyoxal. Various field campaigns have demonstrated the feasibility of good-quality measurements of such gases. However, these were usually performed with custom-tailored instrumentation, and the suitability of these techniques for long-term observations is not yet established. When such substances meet the measurement requirements of GAW, when the usefulness of the substances in providing improved GAW products is demonstrated and when resources are available, these substances will be included in the routine measurement suite.

#### 4. Status of the GAW reactive gases data archive

Stations participating in the GAW Program are required to archive data at the designated World Data Centers (WDC). For reactive gases, this is the World Data Center for Greenhouse Gases (WDCGG, <http://ds.data.jma.go.jp/gmd/wdcgg/index.html>) hosted by the Japan Meteorological Agency, Tokyo, Japan. Station descriptions and other metadata are available from the GAW Station Information System (GAWSIS: <http://gaw.empa.ch/gawsis/>). Measurement data and associated meta-data can be submitted to the WDCGG in various formats and time resolutions. WDCGG staff review data and interact with station personnel and principal investigators in a process to produce final data. Final data are available at hourly time resolution (continuous measurements), at individual sampling times (canister and filter samples), or as longer-term aggregates (i.e. monthly). Overviews of available data products are regularly produced and published in the WDCGG data summary reports (e.g. WMO, 2015). The use of data from the GAW network requires the acceptance of a fair use policy, where each data provider must be contacted and offered co-authorship whenever “substantial use” is made of their data in scientific publications or elsewhere.

Table 1 lists the current status of stations with greater than 60 months of data available through the WDCGG. A month is only counted if at least 67% of the underlying hourly data or flask samples are present and marked as valid. In the following paragraphs we discuss the data availability in more detail.

The earliest data records of continuous measurements of surface ozone in the WDCGG archive are from six sites from the 1970s. Hohenpeissenberg (Germany), and Lisbon (Portugal) commenced measurements with the UV absorption method in 1971. Surface ozone measurements at the NOAA observatories Barrow (Alaska), and Mauna Loa (Hawaii) began in 1973, and South Pole and Samoa followed in 1975. Data from 24 additional stations in Australia, Canada, Japan, Portugal, South Africa, Spain, Sweden, Switzerland, Bermuda, and Barbados commenced during the 1980s. After GAW was initiated in 1989, the number of stations in the global network of surface ozone measurements grew rapidly. Data from 64 stations are available for the year 2000. Presently, according to GAWSIS, surface ozone is measured at 157 GAW stations worldwide. Unfortunately, not all of these data are being submitted to the data center regularly. The WDCGG dataset is complemented by various regional networks who maintain their own data archiving and distribution centers. This sometimes leads to confusion with data users, for example if a station contributes both to GAW and a regional network, and if the data submission procedures between the two data centers are not harmonized.

$\text{CO}$  measurement results archived at the WDCGG have become increasingly available since the early 1990s. Altogether, more than 100 GAW stations are listed in GAWSIS as measuring  $\text{CO}$ , and the data archive contains multi-year records of 23 “Global” and 62 “Regional” stations.

VOC data included in the WDCGG archive have recently been expanded through inclusion of some earlier records, including data from the Pacific transect UC Irvine program, and selected EMEP data sets. Currently, six stations report hourly to daily mean in-situ observations (see section 3.3). Flask data are submitted from ~60 active sites, with flask data time resolution spanning from weekly samples to 4 samples per year. The most extensive records are available for the light  $\text{C}_2$ – $\text{C}_6$  n-alkane hydrocarbons and acetylene. Data for larger molecules, including longer chain VOC and aromatic compounds are available from some of the in-situ sites, such as Hohenpeissenberg, Germany. Older data from the European EUROTRAC-TOR project (1989–1994) are available at <http://ebas.nilu.no>.

$\text{NO}_x$  data are currently limited to 3 Global and 9 Regional stations (Table 1). However, there are several stations which measure and report only  $\text{NO}_2$ . The WDCGG archive holds  $\text{NO}_2$  data of some 30 European GAW stations plus Cape Verde (Republic of Cabo Verde), La Palma (Cuba), Bukit Koto Tabang and Jakarta (Indonesia).

$\text{SO}_2$  data in the archive cover more than 50 stations. Again, these are exclusively European stations with the only exceptions being Bukit Koto Tabang and Jakarta, and Cairo (Egypt). Many of the  $\text{NO}_x$  and  $\text{SO}_2$  time series end around the year 2005 or earlier, and only about half of the stations still submit data regularly. Clearly, efforts are needed not only to expand the actual measurement network for these compounds, but also to improve the completeness of the data in the archive.

As described above, the WDCGG at the Japan Meteorological Agency hosts the Reactive Gases data of GAW. It is envisioned, however, that the responsibility for the Reactive Gases will be transferred to the GAW World Data Center for Aerosols (hosted by NILU, Norway). This change of responsibilities will be gradually implemented in close dialog with data providers and other stakeholders.

## 5. Use of GAW data in science studies

Reactive gases data from the GAW network have been used in a large number of scientific studies including review articles, trend analyses, process studies, and the evaluation of chemistry climate models. It is not always easy to identify the use of GAW data in scientific publications, because the fair use policy of GAW contains no strict requirement to acknowledge the program as such. A systematic review of the science achieved with GAW reactive gases observations is beyond the scope of this paper, but the following paragraphs are intended to provide some insight into the breadth of topics that have been addressed.

Surface ozone measurements from the GAW network have been used extensively in global and regional trend analyses (e.g. Oltmans et al., 2006, 2013; Vingarzan, 2004; Helmig et al., 2007; Gilge et al., 2010; Logan et al., 2012; Parrish et al., 2012, 2013; Cooper et al., 2014). The data, in combination with global-scale chemical transport models, have advanced our understanding of the tropospheric ozone budget and trends. Logan et al. (2012), Parrish et al. (2012), and Oltmans et al. (2013) reported that tropospheric ozone mole fractions in the Northern Hemisphere almost doubled between the 1950s and 2000. Oltmans et al. (2006) used selected surface ozone and ozone sonde measurements to derive global tropospheric ozone trends between the 1970s and 2003/2004. While they found a systematic increase of lower to mid tropospheric ozone mole fractions in the Southern Hemisphere, the patterns in the Northern Hemisphere varied substantially both geographically and temporally. This work showed the apparent stagnation of Northern Hemisphere mid-latitude ozone trends during the late 1990s. Gilge et al. (2010) evaluated 13 years of ozone measurements at four locations, and CO, and NO<sub>2</sub> observations at two high-altitude stations in Europe. While the CO and NO<sub>2</sub> mole fractions decreased between 1995 and 2007, a slight increase in ozone mole fractions was observed at three of the four sites. Logan et al. (2012) also investigated ozone trends over Europe and compared the data from alpine surface sites with aircraft and sonde measurements. Their study documented the improved consistency among the different data sets after 1998 when the GAW program was initiated. This emphasizes the need for well-managed quality control procedures. In contrast to Gilge et al. (2010) they detected a small decrease of ozone mole fractions over Europe after 1998. Parrish et al. (2012) compared data from six European, two North American, two Japanese, and two oceanic sites together with some aircraft data for long-term ozone changes in the Northern Hemisphere mid latitudes. They concluded that surface ozone mole fractions almost doubled between the 1950s and 1990s, stopped increasing over Europe around the year 2000 and over Japan about 5 years later, and continued to rise over the US West coast of the Pacific. In their 2013 study, Parrish et al. reported changes in the seasonal cycles of surface ozone records in Europe and North America which they attribute in part to changes in the spatial distribution of ozone precursors in recent years. The extensive review of Cooper et al. (2014) largely confirms the findings of Logan et al. (2012) and Parrish et al. (2012), but extends their analysis to other world regions. Cooper et al. (2014) found that the subtropical Pacific mountain station Mauna Loa (at 19° N) shows increasing ozone mole fractions that are consistent with trends in East Asia, while Samoa (at 14° S) and South Pole exhibit no significant change over time. Galbally et al. (2011) showed a significant long term increase in surface ozone at Cape Grim (at 41° S) from 1982 to 2010, but no significant increases in ozone in the free troposphere from 3 Australian ozonesonde stations at 38° S, 54° S, and 67° S.

Ozone observations at GAW stations have also been used to explain air pollution signatures at more polluted sites in the same region (for example Galbally et al., 1986; Combrink et al., 1995; Nzotungicimpayea et al., 2014), or for placing intensive field campaign measurements in a longer-term context (for example Murayama et al., 1992; Trainer et al., 1993; Biesenthal et al., 1998; Handisides et al., 2003; Acker et al., 2006; Bartenbach et al., 2007; Hock et al., 2008). Dubois et al. (1997) characterized the regional representativeness of the GAW station Cap Arkona (Germany) by comparing the station measurements with retrievals from a long-path differential optical absorption instrument. A comprehensive assessment of representativeness of a large number of GAW stations in Europe was performed by Henne et al. (2010).

The use of GAW ozone data for the evaluation of (primarily global) chemistry transport and chemistry climate models is demonstrated for example in Stevenson et al. (2006), Fiore et al. (2009), Parrish et al. (2014), and Emmons et al. (2015). These studies identified some systematic biases and inconsistencies between observed and modeled tropospheric ozone mole fractions. Many models exhibit biases in summertime ozone concentrations in the northern mid latitudes, some fail to reproduce seasonal maxima in spring where these occur, and no model has been able to reproduce the observed long-term increase in northern hemispheric ozone before the late 1990s. We note, however, that multi-model studies so far primarily used either regionally aggregated data or data from few selected sites, and that robust procedures for data selection have yet to be developed.

The impact of reactive halogens on boundary layer ozone concentrations in the Arctic was reported by Barrie et al. (1988) and Bottenheim et al. (1990) based on the measurements at the (now) GAW station Alert. Galbally et al. (2000) were later able to identify a potential role of halocarbon species in the mid latitude marine boundary layer using multi-year Cape Grim surface ozone data. Boylan et al. (2015) compared shipborne marine boundary layer ozone data with surface ozone measurements from four coastal and island GAW stations. Their analyses of diurnal ozone cycles suggest an even more enhanced influence of halogen chemistry over the ocean in comparison to the island/coastal-based observations.

There are fewer studies on trends in other reactive gases. Bottenheim et al. (1994) analyzed surface ozone and peroxyacetyl nitrate trends at Egbert, Canada, and found significant differences between the two which they explained with possible changes in the VOC emissions in North America. Numerical model evaluation with GAW VOC data was conducted by Pozzer et al. (2010). A review of VOC trend analyses was reported by Helmig et al. (manuscript in preparation for this special issue).

The distribution and trends of near-surface carbon monoxide mole fractions were analyzed by Novelli et al. (1994, 1998, 2003). They identified the impact of anthropogenic activities in the northern mid-latitudes on the atmospheric composition in the Arctic region. The strong inter-hemispheric gradient and its seasonal cycle were also documented. The observed downward trends in the Northern Hemisphere were attributed to emission controls in North America and Europe. No significant trend was found in the Southern Hemisphere.

Examples for the use of nitrogen oxide observations are largely limited to Europe and the US. Kaiser et al. (2007) used the  $\text{NO}_x$ , CO, and ozone data of the four GAW “DACH” sites (Sonnblick, Zugspitze, Hohenpeissenberg, and Jungfraujoch) and from Mt. Kravac (Slovenia) for identifying air pollutant transport from regional sources by trajectory residence time statistics. Val Martin et al. (2008) analyzed long-range transport from the North American continent based on four years of data from the Pico Mountain Observatory (Azores, Portugal). Gilge et al. (2010) compared  $\text{NO}_2$  time series at Jungfraujoch and Hohenpeissenberg and found similar decreasing trends at both sites, indicative of a large spatial representativeness. Measured trends and trend estimates from emission data by the European Environmental Agency agreed for the SE wind sector at JFJ (influenced by Po Valley) Jungfraujoch. A slightly increasing trend was found at Hohenpeissenberg in the NE sector (city of Munich with increasing population and traffic), and slightly decreasing trends at both sites in the less polluted wind sectors (NW and WSW). The latter were smaller than the expectation based on European emission reductions. Generally, in Europe and North America measurements from air quality monitoring networks show significant reductions of  $\text{NO}_x$  mole fractions in urban and suburban environments in response to emission reductions (Pandey-Deloal et al., 2012; Tong et al., 2015). In contrast, satellite observations indicate that the growing economies in East Asia and the Middle East have led to increasing  $\text{NO}_x$  burdens in those parts of the world (e.g. Hilboll et al., 2013; Mijling et al., 2013). The few GAW stations measuring  $\text{NO}_x$  outside Europe don't exhibit any clear trend signal (WMO, 2015). A combined dataset covering several ground-based networks and other platforms could be very valuable in order to achieve a better understanding of the distribution and trends of this important ozone precursor.

GAW reactive gases measurements have supported various studies on oxidative processes in the lower atmosphere. For example, Atlas et al. (1992), Liu et al. (1992), and Ridley et al. (1992) used the Mauna Loa GAW station to conduct two major atmospheric photochemistry experiments exploring and quantifying the physical chemistry basis of background atmospheric photochemistry. Ayers et al. (1992, 1996) investigated the photochemistry of peroxides in the marine boundary layer in conjunction with surface ozone observations from Cape Grim, Australia. Monks et al. (1998) undertook an extensive experimental study of ozone photochemistry, including radicals, at the same site, while Carpenter et al. (1997) contrasted Cape Grim peroxy radical measurements with observations at the GAW station Mace Head, Ireland. Multi-year measurements of  $\text{H}_2\text{SO}_4$ , OH, and peroxy radicals were carried out at Hohenpeissenberg (Berresheim et al., 2000; Rohrer and Berresheim, 2006) and used in various scientific analyses (for example Birmili et al., 2003; Mannschreck et al., 2004; Mikkonen et al., 2011). Lee et al. (2009) studied the critical  $\text{NO}_x$  limits for chemical ozone production at Cape Verde and their dependence on air mass origin.

## 6. Concluding remarks

Since its inauguration in 1989, GAW has coordinated an extensive global network of high-quality reactive gases measurements. The emphasis on network-wide standards for data quality has led to better comparability of measurements among GAW partners. GAW has provided opportunities for the research community to develop a global perspective on the distribution and trends of reactive gases in the lower atmosphere through its growing archive of measurements. In spite of the great success of GAW, large gaps remain in the global coverage of surface observations. It remains a continuing challenge to maintain the stations and the network-wide quality control.

The current reactive gases program within GAW focuses on ozone, CO,  $\text{NO}_x$ ,  $\text{SO}_2$ , and selected VOCs. In its next phase, the GAW reactive gases program is strengthening its efforts to connect to other existing *in-situ* measurement networks, both ground-based and airborne, and in the future the link with remote sensing data



shall also be strengthened. Additional substances have been identified for which monitoring could provide new insights into the chemistry of the atmosphere and the reasons for observed changes. Numerical modeling will become an integral part of GAW activities as the new GAW implementation plan targets applications instead of focusing on the observation of individual species.

GAW reactive gases data have been used extensively in previous analyses of global and regional atmospheric composition. The surface ozone data set from the WDCGG will form an important component of the Tropospheric Ozone Assessment Report (TOAR; <http://www.igacproject.org/TOAR>) which has recently been endorsed as an activity under the International Global Atmospheric Chemistry (IGAC; <http://www.igacproject.org/>) initiative.

The reactive gas measurement network provides unique and essential data for model evaluation. There are clear opportunities for GAW to further contribute to the ongoing Stratospheric Processes and their Role in Climate (SPARC; <http://www.sparc-climate.org/>)/IGAC Chemistry–Climate Model Initiative (CCMI; <http://www.met.reading.ac.uk/ccmi/>), especially for evaluating the 1960–2010 hindcast runs that are the focus of this year's CCMI activities. Active engagement by GAW representatives in the ongoing CCMI exercise will benefit the GAW and CCMI communities by strengthening the use of observations for model evaluation.

Recently, there has been increasing demand for reactive gases data that are delivered with fast turnaround times to be used for the validation of global atmospheric composition forecasting systems. The European Monitoring Atmospheric Composition and Climate (MACC) project, precursor to the European Copernicus Atmospheric Monitoring Service (<http://www.copernicus-atmosphere.eu/>), is such a system and GAW regularly contributes important data to MACC (e.g. Wagner et al., 2015).

The GAW program will continue to work with the scientific community to make best use of the long-term observations. Continued support by national agencies for existing measurements and further expansion in regions poorly represented are needed for improved understanding of the role of reactive gases in the atmosphere. Optimized data flow, improved data documentation and more near realtime delivery of reactive gases data will create additional use of GAW observations in scientific and operational applications. Active data sharing and intense scientific use of the data will hopefully increase the awareness of the need to maintain and expand global reactive gases observations in the background atmosphere.

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### Contributions

- Contributed to conception and design: MGS, HA, JB, BB, IEG, SG, DH, HK, AL, PN, CPD, TR, MS, RS, OT, KT, VT, CZ
- Contributed to acquisition of data: MGS, HA, JB, IEG, SG, DH, HK, AL, PN, CPD, MS, CZ
- Contributed to analysis and interpretation of data: MGS, IEG, SG, DH, RS, CZ
- Drafted and/or revised the article: MGS, BB, IEG, SG, DH, HK, AL, PN, CPD, TR, MS, RS, OT, KT, VT, CZ
- Approved the submitted version for publication: MGS, HA, JB, BB, IEG, SG, DH, HK, AL, PN, CPD, TR, MS, RS, OT, KT, VT, CZ

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### Competing interests

The authors have declared that no competing interests exist.

### Data accessibility statement

All data that are described or referred to in this article are available from the World Data Center for Greenhouse Gases (WDCGG; <http://ds.data.jma.go.jp/gmd/wdcgg/>). The data associated with the GAW program are available free of charge for non-commercial and scientific use. By using this data, the data user accepts that an offer of co-authorship will be made through personal contact with the data providers or owners whenever substantial use is made of their data. In all cases, an acknowledgement must be made to the data providers or owners and to GAW when these data are used within a publication.

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